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Opinion Article

Plasma assisted combustion: Progress, challenges, and opportunities

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1. Introduction

Increase of energy efficiency and emission reduction are among the most important solutions of sustainable energy [1]. In ground transportation, new engine technologies, such as the Homogeneous Charge Compression Ignition (HCCI), Partially Premixed Compression Ignition (PPCI), and the Reactivity Controlled Compression Ignition (RCCI), work at higher compression ratio and lower combustion temperature, and thus rely more on volumetric ignition than flame propagation in conventional engines. As such, accurate control of ignition timing is critical to control emissions and engine knocking. Unfortunately, most of the existing ignition control methods such as dual fuel or high fuel stratification are passive and difficult to be applied in a broad range of engine loads. Therefore, an active and rapid ignition control method is needed. In stationary power generation, lean premixed high hydrogen content (HHC) syngas combustion is used to meet the NO_x emission target of 2 ppm of gas turbine engines [2,3]. However, ultra lean premixed HHC fuel combustion suffers from severe flame instability, flashback, and blow-off. Moreover, large variation in the energy density (5–80 MJ/kg) of alternative fuels further complicates the problem. Therefore, a new method to extend the lean flammability limit and improve ignition and flame stability is needed.

Plasma, the fourth state of the matter, provides new dimensions for combustion and emission control. These new dimensions include fast thermal heating (the Joule effect), high electron energy (1–100 eV), highly non-equilibrium in electronic and vibrational excited states, and the *Coulomb* and Lorentz forces. As shown in Fig. 1, plasma can modify combustion processes in several different ways [4]. The first enhancement pathway is the thermal one. Plasma can rapidly raise mixture temperature via energy transfer from electrons to neutral molecules and accelerate chemical reaction rates governed by the Arrhenius law. The second enhancement pathway is the kinetic one in which plasma produces high energy electrons and ions as well as electronically and vibrationally excited molecules (e.g., O_2^+, $N_2(*)$,$O_2(^1\Delta_g)$, and $N_2(v)$) and thus leads to the subsequent production of active radicals and reactive species (e.g., O, OH, H, HO_2, O_3, and NO) to accelerate and/or create new chain-initiation and branching pathways. The third enhancement pathway is the direct fuel decomposition by electron impact dissociation, in which large fuel molecules are broken/reformed into small ones and thus modify the fuel reactivity and increase the fuel diffusivity of the mixture. The fourth pathway is the transport enhancement due to plasma generated ionic wind, hydrodynamic instability, and flow motion via the *Coulomb* and Lorentz forces, changing local flow velocity and increasing flow turbulization and mixing.

In the last two decades, plasma assisted combustion has been demonstrated as a magic and promising technique to enhance combustion in internal combustion engines, propulsion systems, emission reduction, and fuel reforming [4–12] by using both equilibrium plasma such as plasma torch and spark plug [13,14] as well as non-equilibrium plasmas such as filamentary discharge [15], corona [16], microwave discharge [17], streamer discharge [18], surface discharge [19], and nanosecond pulsed repetitive discharge [20]. Although many of these experiments demonstrated promising results of combustion enhancement, they often raise more questions than answering the questions. For example: (1) is the observed enhancement due to thermal or kinetic effect? (2) Can non-equilibrium plasma enhance flame speed and extend flammability limit kinetically? (3) Does plasma enhance low temperature chemistry more than high temperature chemistry? (4) What kinds of plasmas are the best options for applications? (5) Is the observed enhancement caused by non-uniform multi-dimensional discharge effects?

2. Progress of plasma assisted combustion

To address above questions, experiments of plasma assisted combustion (PAC) have been conducted by using uniform discharges in well-defined ignition and flame geometries such as flow reactor [21], shock tubes [5,6], counterflow flames [22,23]) using advanced laser diagnostics [24–26]. These progresses can be summarized in four categories.

The first major progress in PAC was the finding of significant extension of the explosion limit, engine lean burn limit, and flame lean blow-off limit. The uniform nanosecond pulsed plasma discharge (NSP) in shock tube experiments demonstrated that plasma can ignite mixtures far below the explosion limit [27–30]. The subsequent engine tests [31,32] showed that microwave discharge extended engine lean burn limit by 20–30% with a small (50 mJ) energy input. Recent flame experiments [9,33–35] also revealed that flame stabilization, ignition, and extinction limits can also be extended by PAC.

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The second major progress is the advancement of fundamental understanding of the kinetic process of plasma assisted combustion. Direct atomic O measurements [21,11,24] in plasma discharge showed that O production from O_2 collisions with hot electrons, excited nitrogen ($N_2(A)$, $N_2(B)$, and $N_2(C)$), and ions are the major pathways for radical production for PAC at low temperature.

The third major advance of plasma assisted combustion is the findings of plasma assisted cool flames and the direct ignition to flame transition without an extinction limit [20,36] (Fig. 2). The direct ignition to extinction transition (Fig. 2) reveals that plasma can enhance ignition much more greatly than that to flame stabilization. Moreover, plasma enhances low temperature ignition more than that to high temperature ignition and can create a new plasma assisted low temperature combustion regime. Based on this finding, self-sustaining dimethyl ether (DME) and n-heptane cool flames [23,36] were established by using direct plasma discharge and plasma generated ozone addition. This non-equilibrium plasma activated low temperature combustion may lead to a new technique to control engine ignition and fuel reforming (Fig. 2).

The fourth advance in plasma assisted combustion is the understanding of the mechanism of the reduction of the minimum ignition energy and flame initiation time by plasma. The minimum ignition energy has been found to be governed by a critical flame initiation radius [37,38], which is a strong function of the mixture

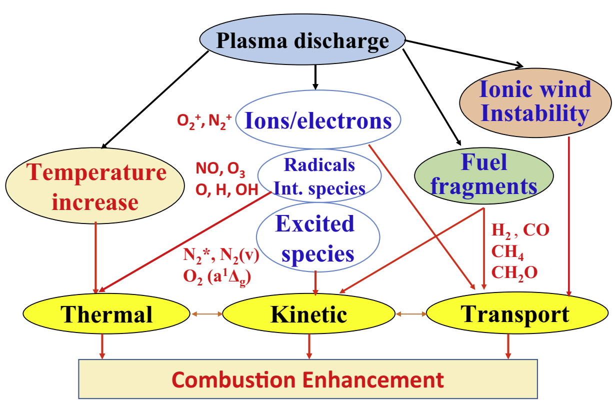

Fig. 1. Four combustion enhancement pathways of plasma assisted combustion [4].

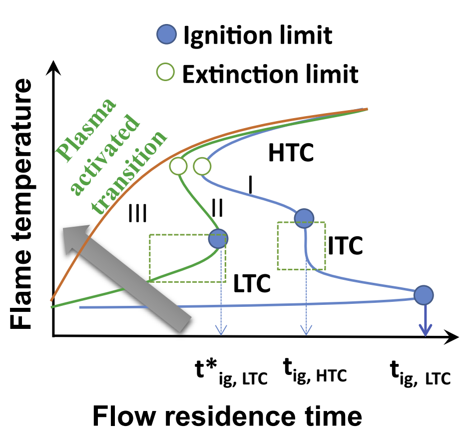

Fig. 2. Plasma activated low temperature ignition and flame regime transition from the conventional *S*-curve (I: no plasma) with separated ignition and extinction limits to a monotonic transition curve from ignition to ignition without extinction limit (III) ignition to flame transition curve without extinction limit (III: strong plasma kinetic effect). HTC: high temperature combustion, ITC: intermediate temperature combustion, LTC: low temperature combustion.

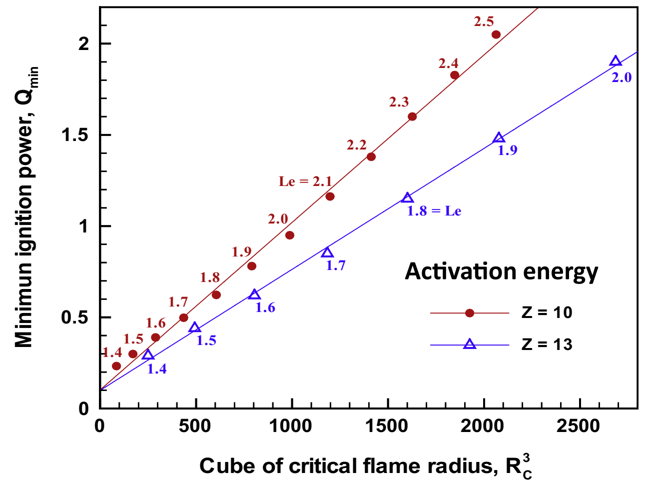

Fig. 3. Dependence of the minimum ignition energy on critical flame initiation radius (R_c^3) for different mixture Lewis numbers (Le), and activation energy (*Z*) [37,38].

Lewis number, fuel reactivity (activation energy), and flame thickness (Fig. 3). It was found that even if the mixture is above the flammability limit, if the plasma discharge cannot drive the ignition kernel up to the size of the critical radius, ignition will fail. Therefore, non-equilibrium plasma can reduce the minimum ignition energy and shorten flame initiation time in engines by breaking the large fuel molecules into small ones to reduce the Lewis number, modifying the fuel chemistry, and increasing the ignition volume so that the ignition kernel size is greater than the critical flame initiation radius.

3. Opportunities, challenges, and future research

For internal combustion engines, one opportunity is to use a large volume ignition by non-equilibrium plasma discharge to reduce ignition time and enable leaner combustion. Another opportunity is to increase engine efficiency and suppress knocking by using volumetric plasma assisted ignition to actively control the low and high temperature ignition timing in advanced engines using high octane number of fuels. The major challenge is the difficulty to generate large volumetric discharge at high pressure. Nevertheless, plasma can effectively generate chemically active species such as ozone, H_2O_2, and singlet oxygen at high pressure and low temperature, which may provide new opportunities to actively control engine ignition.

For gas turbine and scramjet engines, non-equilibrium plasma discharge can significantly enhance ignition and improve flame stabilization (Fig. 2). In stationary power generation, the combination of a microtube array combustor with non-equilibrium plasma may have the potential to solve both problems of flame flashback and lean blow-off with ultra lean HHC fuels. In addition, the combination of microwave with gliding arc and short pulse discharge can be used to stabilize gas turbine combustion of fuels with very low heating values. Moreover, large volume ignition by non-equilibrium plasma is a promising technology to resolve the failure of afterburner relight, and promote ignition and selective fuel reforming of endothermic fuels in scramjet engines. The key challenge is how to produce discharge in the regions of fuel air mixing which is away from the electrodes with low energy cost and pressure loss.

In fuel processing and emission control, plasma can accelerate fuel oxidation, ignition, and even cool flames at lower temperature and lower pressure. Therefore, non-equilibrium plasma may be used to develop plasma assisted flameless combustion at lower

temperature to further reduce NO_x. In addition, plasma generated cool flames and low temperature fuel oxidation can be used for *in situ* fuel reforming and production of valuable chemicals. Moreover, atomic O production by plasma can be used to remove and oxidize soot, coke deposit, unburned or trace hydrocarbons, and toxic organic materials.

However, Understanding the kinetic process of PAC is very challenging. The state of the art approach to model the chemistry of plasma assisted combustion is to use a combined air plasma chemistry and conventional kinetic mechanism of combustion [39]. However, for low temperature plasma assisted ignition (300–900 K) [40], the existing air plasma mechanism together with combustion mechanisms (e.g. HP Mech [40] and USC-Mech [41]) fails to predict the species production even for H_2O and CH_4 in nanosecond repetitively pulsed discharge for ethylene/oxygen mixtures. At low temperature, the plasma activated low temperature oxidation pathway is dominant. However, plasma assisted low temperature oxidation kinetics has been poorly studied. Few quantitative validation data are available, especially for liquid fuels. Unfortunately, understanding of the kinetics of PAC is a daunting challenge due to large span of timescales in addition to large number of active species. For example, the electron impact energy transfer and molecule excitation process are very short (within 100 ns). However, the energy transfer between the excited species and neutral molecules of reactants as well as the low temperature fuel oxidation occur in a broad range of timescales (100 ns–1 s). Many kinetic processes involving energy transfer between the excited species and neutral molecules of reactants are not well understood. Firstly, the quenching rates and pathways of electronically excited states of nitrogen and oxygen by hydrocarbons and combustion products are not well-known. Secondly, the reaction rates of ion, vibrationally-excited molecules, and ozone with hydrocarbon fuels are also poorly understood. Thirdly, the energy transfer and coupling between molecules with different excitation modes need to be further investigated. Fourthly, the cross-section areas of electron impact energy transfer for large molecule fuels such as n-heptane and iso-octane as well as their intermediate species are lacking. And finally, the low temperature fuel oxidation with plasma activation and excited species between 300 K and 900 K are poorly examined. Both high level *ab initio* quantum chemistry computation and experimental measurements of elementary reaction pathways and rate constants are urgently needed.

Experimental studies of plasma assisted combustion kinetics are also facing several challenges. Firstly, measurements the local electric field strength (E/N) and electron number density and temperature are needed to validate kinetic models. Secondly, establishment of uniform discharge at high pressure for kinetic study remains challenging. Few high quality experimental data at high pressure are available. Thirdly, *in situ* measurements of time histories of intermediate species such as RO_2, HO_2, H_2O_2, CH_3, C_2H_3, CH_2O, O_3, and aldehydes in addition to O, H, OH and excited species in a flow reactor, shock tube, and rapid compression machine are necessary to understand the low temperature oxidation and pathways. Finally, development of experimentally validated high pressure plasma assisted combustion kinetic mechanism is needed.

Another challenge is PAC modeling. The conventional method is to use an estimated plasma field strength (E/N) and electron number density to calculate electron energy distribution and the rate constants of electron impact excitation, dissociation, and recombination reactions. Although such approach is computationally efficient, it is highly dependent on the estimated/guessed plasma properties. Therefore, it is necessary to compute the electric field strength and electron number density from the experimental parameters. Unfortunately, such computations are not only computational expensive but also difficult to converge if the quenching processes of electrons and excited species are not appropriately included. Moreover, it is difficult to solve the sheath energy and charge accumulations on the electrodes. Furthermore, an adequate description of multidimensional plasma discharge is even more challenging.

Nevertheless, progress has been made to actively control PAC by using lasers to guide and localize the plasma discharge in a reacting low. For example, by using a femtosecond laser [42,43], the discharge pattern and the channel location of plasma filamentary discharge can be controlled. The increase of controllability of plasma discharge may contribute significantly to the design of large volume plasma discharge at high pressure.

4. Conclusion

Non-equilibrium plasma assisted combustion is a promising technology to improve engine efficiency, reduce emissions, and enhance fuel reforming. Over last years, several significant progresses have been made towards the understanding of the plasma magic and its underlying chemistry and dynamic processes via advanced diagnostics, combustion chemistry, and theory. New observations of plasma assisted ignition enhancement, ultra-lean combustion, flameless combustion, cool flames, and plasma discharge control are reported. These findings open new opportunities to develop predictive kinetic models and modeling tools for plasma assisted combustion at low temperature and high pressure and in the development of efficient plasma discharges for practical applications. There are still a large gap in developing high pressure volumetric discharge systems for application and predictable models and tools for quantitatively simulating plasma assisted combustion.

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